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Covalent Bonding of Organic Molecules to Cu and Al Alloy 2024 T3 Surfaces via Diazonium Ion Reduction

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Cu surfaces and polished aluminum alloy 2024 T3 substrates were derivatized at open-circuit potential with aryl diazonium salts in both aprotic and aqueous media. Raman spectroscopy confirmed the presence of a derivatized film on the substrates before and after exposure to boiling water and sonication in acetone. Two different Cu substrate surfaces were prepared and used for X-ray photoelectron spectroscopy (XPS) analysis of the derivatization results. One surface was native oxide Cu, predominantly in the form of Cu_2O, and one surface was predominantly Cu^0. Results of the XPS analysis indicate the presence of both a Cu-O-C linkage and a Cu-C covalent bond between the aryl ring and the Cu substrate, and a high coverage of the organic layer. XPS results also indicate the formation multilayers on both types of Cu surfaces with different percentages of azo coupling within the multilayers on the two surfaces. Applications of a covalently bonded organic film on copper and alloy surfaces include adhesion promotion, corrosion protection, and possibly inhibition of oxygen reduction.
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Covalent binding of phenyl groups to carbon surfaces via electrochemical reduction of aryl diazonium salts has led to an interest in similar binding to metal surfaces.[1-10] Such binding has been confirmed on metal surfaces, but the exact nature of the bond is still under study.[1,5] In particular, the similarity of the metal-organic bond to the C-C bond studied extensively on carbon surfaces treated with diazonium reagents has yet to be established. ''Metal'' surfaces are often actually metal oxide surfaces and therefore, the question arises: Does the aryl group bind directly to the metal forming a metal-carbon bond, and/or does it bind to the oxide forming a metal-oxygen-carbon linkage? This question is posed schematically in Fig. 1. Factors that might play a role in the nature of the bond include the identity of the metal, the oxidation state of the metal surface, the thickness of any metal oxide layer, the nature of the R group, and the derivatization conditions. An easy, economical method of covalently bonding a variety of molecules to metal and/or metal oxide surfaces can have a number of applications.

One such application is the replacement of chromate corrosion inhibitors. With the almost endless possibilities for R-groups on aryl diazonium salts, a wide range of adhesion promoters can be obtained from their covalent binding onto a metal surface. Studies with silane-based ormosils are based on the similar idea of attaching organic molecules to metal surfaces to promote adhesion and inhibit corrosion.[11,12] Covalently bonded molecules can potentially occupy both anodic and cathodic sites, possibly preventing anodic dissolution and/or blocking oxygen reduction. The blocking of oxygen reduction is of particular importance in aluminum alloys, in which added copper and other metals provide greatly increased strength.[13-15] Unfortunately, copper alloying also leads to the establishment of local galvanic cells between copper-rich and copper-poor areas and thus destructive localized corrosion.[16,17] Derivatization of Cu sites by organic molecules may reduce localized corrosion by inhibiting both anodic and cathodic processes. The success of chromate as a corrosion inhibitor is due in part to the reductive adsorption of Cr^{VI} to the active cathodic sites, particularly Cu in Cu/Al alloys.[14,18] Organic diazonium ions also chemisorb through reduction to an aryl radical, then formation of a surface-phenyl bond. The fact that Cr^{VI} and diazonium ions are both irreversibly adsorbed via reduction makes the diazonium reagents potentially effective alternatives to chromate. A better understanding of the mechanism involved in the derivatization of a Cu surface with aryl diazonium salts can provide information necessary for choosing a proper set of conditions when testing diazonium salts as corrosion inhibitors. The nature of the bond formed on a Cu substrate derivatized with an aryl diazonium salt, the stability of the bond, the formation of multilayers, and both aprotic and aqueous derivatization conditions are discussed.

In addition to playing a significant role in aluminum alloys, Cu also has a unique history with diazonium salts. The well-known Gattermann and Sandmeyer reactions involve the use of Cu^0 and Cu^{+1}, respectively, to form free radicals from diazonium salts.[19-21] In these reactions copper typically serves as a catalyst, first giving up an electron to the diazonium cation to form the aryl radical and N_2. The oxidized copper then accepts an electron when the aryl radical bonds with a nucleophile, such as Cl^-. The Sandmeyer reaction is the most common method of metal cation-induced diazonium reduction, often referred to as ''dediazoniation''. Waters attributes the success of the Sandmeyer reaction to the compatibility of the reduction potential of Cu^{+1} with the reduction potential of many diazonium salts.[19] The experiments undertaken herein investigate a somewhat similar reaction with Cu^0 and/or Cu^{+1} on the copper surface, providing an electron for reduction of the diazonium cation to form the aryl radical which then reacts with the copper surface.

Experimental

Materials.—The substrate was 99.99% copper foil, 1.0 mm thick, obtained from Alfa Aesar and cut into approximately 1 cm^2 pieces. These Cu pieces were polished as described later and used in that form for all experiments involving a Cu substrate, except the measurement of open-circuit potentials (OCPs). For the purpose of measuring OCPs, a copper wire was attached to one side of a 1 cm^2 piece of Cu with silver epoxy resin (SPI Supplies/Structure Probe, Inc.). The assembly was then embedded in epoxy (Buelher), leaving the smooth side exposed. This copper electrode was hand-polished with successive grits of silicon carbide papers wetted with Nanopure water (Buelher 240, 400, 600) then rinsed in H_2O, sonicated in ethanol for >30 min, and air dried immediately before use.

Phenyl diazonium fluoroborate (phenyl diazonium salt), 4-nitrophenyl diazonium fluoroborate (nitrophenyl diazonium salt), and 4-nitroazobenzene-4′-diazonium tetrafluoroborate (nitroazobenzene diazonium salt) were synthesized from the appropriate amine (Aldrich) using the method previously described as adapted from Starkey.[22,23] 3,3′-Dimethoxybiphenyl-4,4′-bisdiazonium fluoroborate (fast blue diazonium salt) was purchased from Acros Organics. Unless otherwise indicated, reagent-grade acetonitrile (ACN), ether, ethanol, sulfuric acid, and glacial acetic acid were used as received. All water used was Barnstead Nanopure water, 17.8 MΩ cm minimum resistivity.

Instrumentation.—X-ray photoelectron spectroscopy (XPS) spectra and X-ray stimulated Auger spectra were acquired with a

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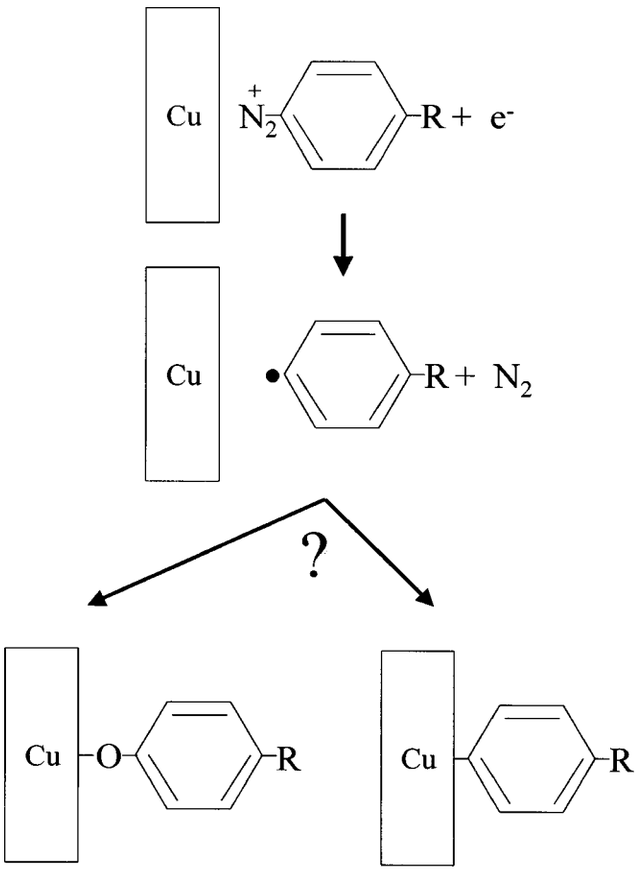

Figure 1. Binding of aryl ring to Cu substrate.

Kratos Axis Ultra electron spectrometer using a monochromatic Al Kα source, power of 140 W, pass energy of 20 eV (80 eV for survey spectra), hybrid magnification (both electrostatic and magnetic), step size of 0.1 eV for all spectra, analysis area of 700×300 μm, take-off angle of 90° relative to the surface, and an analysis chamber pressure of $<5 \times 10^{-9}$ Torr. In addition to a survey spectrum for each sample with a binding energy (BE) range of 0-1000 eV, spectra were acquired for individual elements with minimum BE ranges of: C 1s, 280-296 eV; Cu 2p, 928-970 eV; O 1s, 528-537 eV; N 1s, 390-410 eV. Auger spectra of the Cu LMM line were acquired with a minimum kinetic energy (KE) range of 907-927 eV. A minimum of five scans per spectrum was performed for the individual element XPS spectra and the Auger spectra. Survey spectra were acquired with one scan. The BE scale was calibrated with the established C 1s peak for adventitious carbon on both copper and copper oxide surfaces (284.7 eV).[24] Samples derivatized in the diazonium solution for long periods of time (15 min) exhibited spectral shifts due to charging in the thicker films. These spectra were calibrated using the C 1s peak arising from carbon in the phenyl ring that appeared at 284.75 ± 0.05 eV on all spectra of samples derivatized for 1 min or less.

Raman spectra were acquired with a 514.5 nm laser on an f/1.5 Kaiser spectrograph with a holographic grating, 180° backscattered geometry, and a laser spot size of ~50 μm. The spectrograph was equipped with a liquid-nitrogen-cooled charge-coupled device (CCD) detector operating at −110°C. A video CCD camera was used to focus the laser at low power (<200 μW). Spectra were acquired with 5 mW of laser power at the sample and intensities were not corrected for instrumental response. All spectra were acquired with an integration time of 20 s or less.

OCPs were measured on a Gamry PC3/300 workstation. The cell used for OCP measurements consisted of the above-described Cu working electrode, a Pt wire counter electrode, and either a Ag/AgCl or a Ag/Ag^+ reference electrode in 30 mL of 100 mM aqueous H_2SO_4 or ACN, respectively, all contained in a 100 mL beaker. The cell was stirred with a magnetic stirring bar during these measurements. The $E_{1/2}$ of ferrocene in ACN was observed at +90 mV *vs.* a Ag/Ag^+ reference electrode (BAS). Measurements obtained with a Ag/AgCl (aq) reference electrode (BAS) were adjusted to values relative to the Ag/Ag^+ reference electrode based on a standard electrode potential for ferrocene of +307 mV *vs.* a saturated calomel reference electrode (SCE, aq).[25] (Calculated value: Ag/AgCl = −261 mV *vs.* Ag/Ag^+.)

Sample preparation.— Aprotic derivatization.—Copper samples (1 cm^2) were mechanically polished with successive grits of wetted silicon carbide papers (Buelher 240, 400, 600), rinsed in H_2O, and sonicated in ethanol for >30 min. Immediately before the derivatization process, the Cu samples were rinsed in fresh ethanol and air dried. Two different derivatization processes were employed, one in which the Cu was derivatized in its native oxide state and one in which copper oxide was removed from the Cu surface before derivatization. These two states are referred to as ''native oxide Cu'' and ''bare Cu'', respectively. The pretreatment used to remove copper oxide from the surface consisted of immersing the Cu sample in unpurged acetic acid for 30 s.[26] The derivatization solutions consisted of only the diazonium salt and the solvent, either 100 mM aqueous H_2SO_4 or ACN. The derivatization process for native oxide Cu consisted of: (*i*) 5 s rinse in ACN, (*ii*) timed dip in a stirred 3 mM solution of the specified diazonium salt dissolved in ACN, (*iii*) 10 s rinse in fresh ACN, (*iv*) air drying, and (*v*) if used for XPS analysis, introduction into the XPS vacuum transfer chamber within 20 min. The derivatization process for bare Cu was almost identical to that for native oxide Cu but with steps added to remove the oxide and retard its regrowth. During derivatization of the bare Cu all rinsing and derivatization solutions were purged with Ar for a minimum of 15 min before the start of the process and also throughout the process. The derivatization process for bare Cu consisted of: (*i*) 30 s pretreatment in unpurged glacial acetic acid, (*ii*) 5 s rinse in purged ACN, (*iii*) timed dip in a stirred, purged 3 mM solution of the specified diazonium salt in ACN, (*iv*) 10 s rinse in fresh, purged ACN, (*v*) Ar jet drying, and (*vi*) if used for XPS analysis, introduction into the XPS vacuum transfer chamber in <15 s. Control samples for both the native oxide Cu and the bare Cu were prepared as noted in the discussion section. For both the native oxide Cu and the bare Cu, dipping times in the diazonium salt solution varied from 5 to 30 min as indicated later. Both the aprotic and aqueous derivatization procedures are summarized in Table I.

Aqueous derivatization.—Copper samples were polished and sonicated as noted previously and then rinsed in fresh ethanol and air dried immediately before derivatization. The derivatization solution was 1-3 mM diazonium salt dissolved in 100 mM H_2SO_4 in water. The derivatization procedure consisted of simply dipping the Cu samples for the indicated derivatization time in the stirred diazonium salt solution, thoroughly rinsing with water, and air drying.

Data analysis.—Surface atom percentages were calculated in the following manner. Intensities of all XPS spectra were adjusted to counts/s and peak areas were integrated using Galactic's Grams spectral software (Galactic Industries, Salem, NH, Version 4.02). Areas were adjusted using both sensitivity factors and transmission values for the Kratos Axis Ultra. The same energy range of integration was used for each element and was chosen so that it included the entire peak width for that element in all spectra. No curve fitting was employed. Survey spectra indicated that the surface contained measurable amounts of only C, Cu, O, and N. Therefore, total areas for these elements were used to determine the total surface coverage.

Table I. Procedure for aprotic and aqueous derivatization.

Sample	Pretreatment	Rinse	Dip (derivatization)	Rinse	Dry
Aprotic					
Native oxide Cu	···	ACN, 5 s[a]	3 mM diazonium salt in ACN	ACN, 10 s	Air
Bare Cu	Acetic acid, 30 s[a]	Purged ACN 5 s	Purged 3 mM diazonium salt in ACN	Purged ACN 10 s	Ar jet
Aqueous					
Native oxide Cu	···	···	3 mM diazonium salt in 100 mM H_2SO_4 /H_2O[a]	H_2O	Air

[a] All samples were mechanically wet-polished with successive grits of silicon carbide papers (240,400,600), rinsed in H_2O, sonicated in ethanol for >30 m, rinsed in fresh ethanol, and air dried immediately before the first step.

The ratio of phenyl rings/azo group on each sample was calculated using areas (adjusted as noted previously) for the C 1s peak (280-294 eV) and the N 1s peak attributed to azo groups (398-402 eV). The adjusted area for the C 1s peak was divided by six (relative no. phenyl rings) and the adjusted area for the N 1s peak was divided by two (relative no. azo groups).

Results and Discussion

Aprotic vs. aqueous derivatization.—Adenier *et al.* demonstrated the controlled potential derivatization of iron surfaces with aryl diazonium salts in both aprotic (ACN) and aqueous (0.05 M H_2SO_4) media.[1] The derivatization processes described herein, however, were performed at OCPs in solutions of diazonium salts dissolved in either 100 mM aqueous H_2SO_4 or ACN and were accomplished by simply dipping the copper samples in the salt solution for a specified period of time. The OCPs of native oxide Cu in both the solvents and the derivatization solutions were measured for comparative purposes using the cell described previously. In both cases, the OCP was measured for approximately 2 min in either 100 mM aqueous H_2SO_4 or ACN (0.1 M tetrabutylammonium tetrafluoroborate was added as an electrolyte to the ACN). After approximately 2 min, phenyl diazonium salt (dissolved in the respective solvent) was added to the stirred cell to bring the final cell concentration of the diazonium salt to 3 mM. Although aqueous potentials were measured against a Ag/AgCl reference electrode, all potentials noted are *vs.* Ag/Ag^+. The OCPs of native oxide Cu in 100 mM aqueous H_2SO_4 and ACN are approximately −350 and −575 mV, respectively. Those potentials increase to approximately −200 and −375 mV, respectively, upon addition of phenyl diazonium salt to a final concentration of 3 mM. (The electrolyte added to the ACN was used only during measurements of the OCP and was not used during the open-circuit derivatization of copper samples discussed throughout this paper. Therefore the OCPs in ACN noted previously should be regarded as estimates of the OCP during derivatization.)

Two different Cu surfaces were derivatized with diazonium salts. One surface consisted mainly of the native oxide formed on a Cu surface and one surface consisted mainly of bare Cu, prepared using the method established by Chavez and Hess.[26] Figure 2 is the X-ray stimulated Auger spectra of both surfaces. In the case of native oxide Cu, the Cu sample was polished, sonicated in ethanol, rinsed in fresh ethanol, air dried, rinsed in ACN and introduced into the XPS chamber within 20 min. The bare Cu was polished, sonicated in ethanol, rinsed in fresh ethanol, air dried, pretreated in acetic acid for 30 s, dipped in purged ACN for 15 min, dried with Ar, and introduced into the XPS chamber within 15 s. Figure 2 shows that the native oxide Cu has its strongest peak at 916.7 eV, while the bare Cu has its strongest peak at 918.6 eV. These values agree with the well-established energies for Cu LMM Auger lines for Cu_2O (916.5 eV) and Cu^0 (918.5 eV), respectively.[26-28] Neither surface is pure Cu_2O or Cu^0, but these species clearly dominate the respective surfaces. The Cu LMM Auger lines for two other likely species, CuO and $Cu(OH)_2$, are at 918.1 and 917.0 eV, respectively.[27,29,30] Furthermore, surface coverage determined by XPS spectra of these underivatized control samples indicate far less oxygen and more copper on the bare Cu sample (Table II).

Aqueous derivatization.—OCP derivatization in both aprotic and aqueous media was shown to be effective. A water-based treatment presents the considerable advantage of easier waste disposal. Sulfuric acid, however, is known to remove copper oxide from copper surfaces and using H_2SO_4 in the derivatization solution would make it difficult to determine the predominant oxidation state of the surface during derivatization.[31] Therefore, for the purpose of determining the nature of the bond established during derivatization, most of the experiments were carried out in ACN solutions. Several native oxide Cu samples were derivatized in the H_2SO_4 solution, however, to establish the viability of open-circuit derivatization in water. Native oxide Cu was derivatized in 3 mM acidic solutions of phenyl, nitrophenyl, nitroazobenzene, and fast blue diazonium salts (struc-

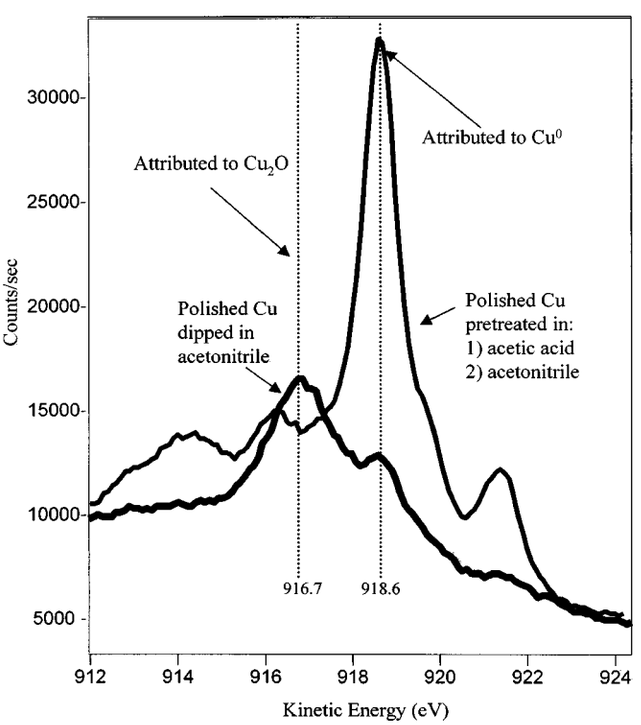

Figure 2. Cu (LMM) Auger spectra of native oxide Cu and bare Cu.

Table II. Surface coverage of samples derivatized with phenyl diazonium salt.

	% O	% Cu	% C	% N[a]
Control native oxide	26	38	36	<1
10 s native oxide dip	25	33	40	1
1 m native oxide dip	26	19	54	1
15 m native oxide dip	11	1	86	2
Control bare Cu	6	71	22	<1
10 s bare Cu dip	12	48	39	1
1 m bare Cu dip	3	1	91	5
15 m bare Cu dip	3	0	91	6

[a] Using the integrated area from 398 to 402 eV, attributed to N in azo groups.

tures shown in Fig. 3) with dipping times varying from 2 to 15 min, followed by a thorough water rinse. For all four salts, Raman spectroscopy confirmed the presence of the respective molecule on the Cu surface (Fig. 4). Samples derivatized with nitroazobenzene and fast blue diazonium salts produced strong spectra, possibly from either surface enhancement or resonance effects.[8] The spectra of the samples derivatized with nitrophenyl and phenyl diazonium salts were not as strong but both still clearly show the well-established phenyl ring carbon-carbon stretch at ~1600 cm^{-1}, and the presence of this peak was easily reproduced on multiple samples derivatized with both salts.[32] As further evidence of the successful derivatization of phenyl diazonium salt in acidic solution, XPS analysis of a native oxide Cu sample derivatized with a 15 min aqueous dip shows a decrease of 97% in Cu coverage and an increase of 107% in C coverage on the sample surface, compared to a control sample of native oxide Cu.

Two separate experiments were performed to test the strength of the bond created during derivatization in an acidic solution. The presence of the carbon-carbon ring stretch at ~1600 cm^{-1} in Raman spectra was used to verify the successful derivatization and persistence of various molecules on the Cu surface. First, a native oxide Cu sample was derivatized by dipping for 2 min in a 1 mM solution of nitroazobenzene diazonium salt in 100 mM H_2SO_4. The sample was then boiled in 75 mL of water for 1 h and air dried. Raman spectra acquired before and after boiling both showed the presence of nitroazobenzene on the surface. The spectrum acquired after boiling, however, showed a 69% decrease in the intensity of the 1600 cm^{-1} band. Furthermore, the band at 1336 cm^{-1} (NO_2 stretch) was severely diminished in the spectrum of the boiled sample. Additionally, a native oxide Cu sample was derivatized by dipping for 2 min in a 3 mM solution of fast blue diazonium salt in 100 mM H_2SO_4. Figure 5 shows the spectra of this sample acquired before and after sonication in acetone for 15 min. Although the intensity after sonication is diminished, it shows that fast blue is still present on the Cu

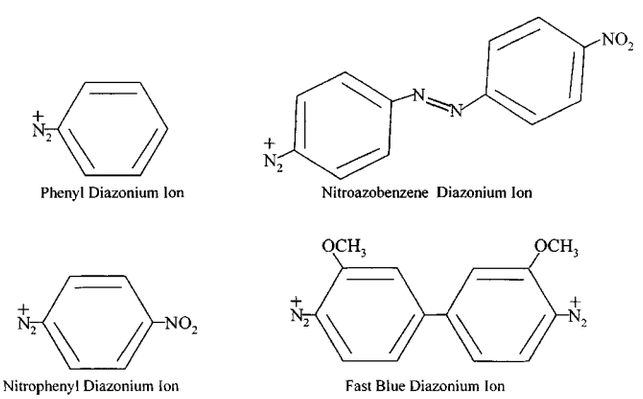

Figure 3. Structures of diazonium ions.

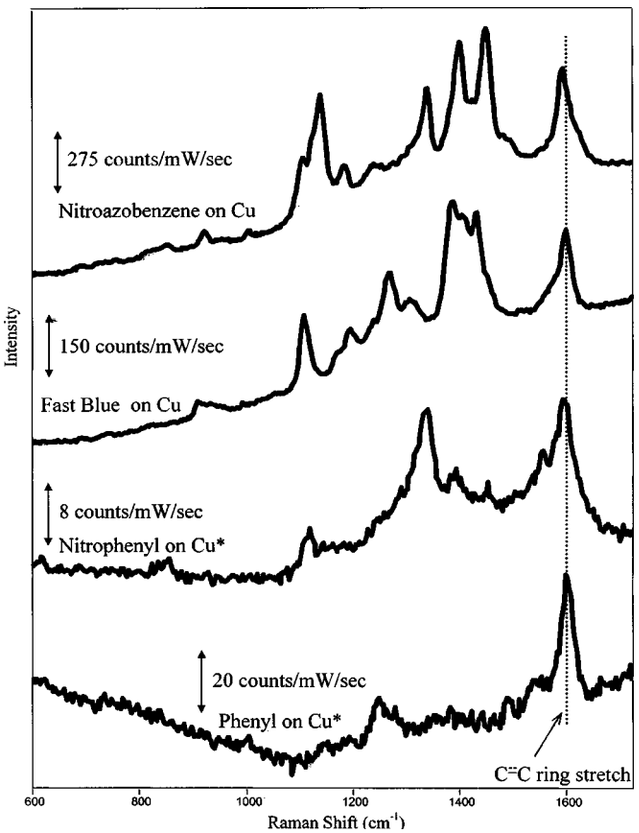

Figure 4. Raman spectra of native oxide Cu derivatized with various diazonium salts in 100 mM H_2SO_4. *Linear baseline subtracted.

surface after an aggressive attempt to remove it. (The choice of diazonium salt for these two tests was arbitrary to the extent that nitroazobenzene and fast blue diazonium salt were preferred over nitrophenyl or phenyl diazonium salt for their strong Raman scattering.)

Although it was not examined in detail, aluminum alloy 2024 T3 was also subjected to open-circuit derivatization in both aqueous and aprotic media with nitroazobenzene diazonium salt. Spectra of samples derivatized under both conditions confirmed the presence of the nitroazobenzene-derivatized layer. Preliminary spectra of polished AA-2024 T3 derivatized at open circuit in 3 mM nitroazobenzene diazonium salt in 100 mM H_2SO_4 are shown in Fig. 6, before and after boiling in water for 1 h. These spectra are virtually identical in both appearance and intensity, although the NO_2 stretch at 1339 cm^{-1} was slightly diminished for the boiled sample.

Aprotic derivatization.—Both native oxide Cu and bare Cu surfaces were derivatized in phenyl and fast blue diazonium salts, respectively, in ACN solutions. Raman spectra of both samples acquired before and after sonication in acetone for 15 min show no difference in the intensity of the carbon-carbon ring stretch at 1605-1608 cm^{-1}, indicating the formation of a strong bond between the phenyl ring and the copper substrate.

Determination of the nature of the phenyl-substrate bond.—All analyses undertaken to determine the nature of the surface bond between Cu and the organic reagent were performed with aprotic solutions. Unless otherwise noted, all derivatization was performed at OCP in 3 mM solutions of phenyl diazonium salt. Phenyl diazonium salt was chosen because it should contribute only to the C 1s XPS spectra and not to the O 1s spectra.

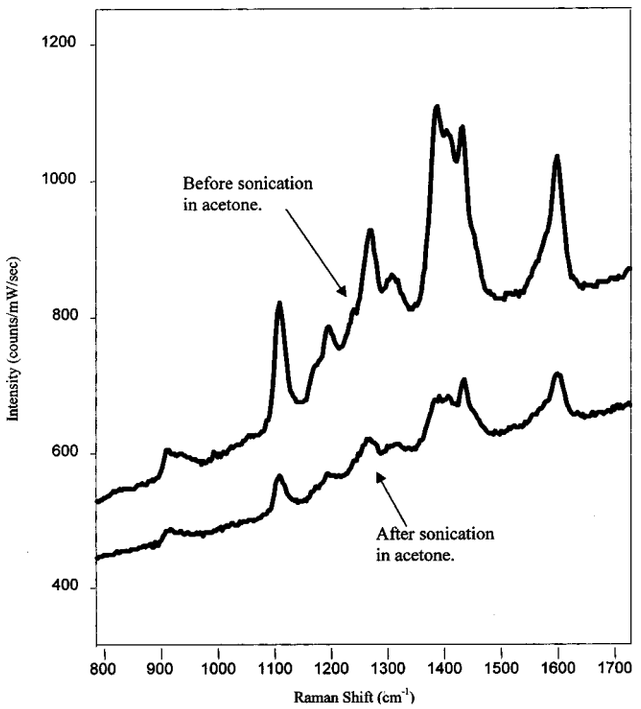

Figure 5. Raman spectra of Cu sample derivatized with fast blue diazonium salt under aqueous conditions both before and after sonication for 15 min in acetone.

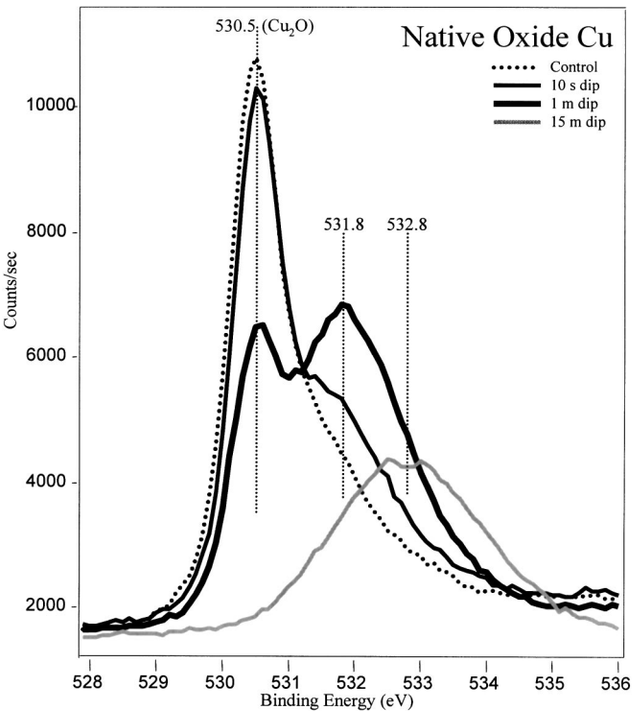

Figure 7. O 1s XPS spectra of native oxide Cu surfaces derivatized with increasing dipping times in phenyl diazonium salt solutions.

Cu-O-C Bond.—Figure 7 shows the O 1s XPS spectra of four native oxide Cu samples, one control sample and three samples derivatized with phenyl diazonium salt. The control sample was polished, sonicated in ethanol for >30 min, rinsed in fresh ethanol, air dried, dipped in ACN for 5 s and air dried. The three derivatized samples (prepared as noted in the Experimental section) were dipped in the diazonium reagent for 10 s, 1 min, and 15 min. All four samples were placed in the XPS vacuum transfer chamber within 20 min of preparation. Cu_2O is expected to be the predominant species on the control sample.[33] The peak at 530.5 eV agrees reasonably with this expectation as the O 1s peak for Cu_2O is at 530.3 eV and the Cu Auger spectrum of this same sample (Fig. 2) indicates a predominance of Cu_2O.[26,30] $Cu(OH)_2$ and CuO with O 1s lines at 530.7-531.2 and 529.6 eV, respectively, most certainly contribute to the spectrum, but the 530.5 eV peak dominates the spectrum of the control sample. With increasing derivatization times, however, the peak moves more positive, reaching a value of 532.8 eV on the sample derivatized for 15 min.

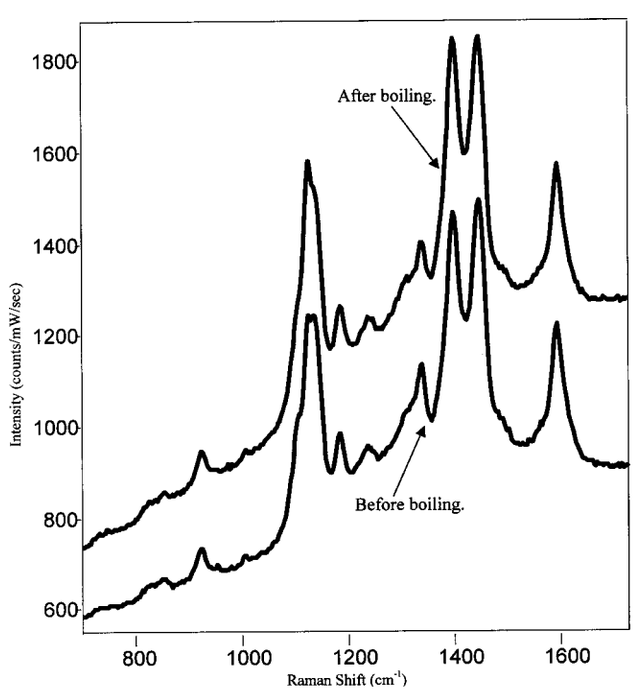

Figure 6. Raman spectra of AA-2024 T3 sample derivatized with nitroazobenzene diazonium salt under aqueous conditions both before and after boiling in water for 1 h.

Figure 8 is the O 1s spectra of bare Cu samples, one control sample, and three samples derivatized (as noted in the Experimental section) for 10 s, 1 min, and 15 min in phenyl diazonium salt solution. The control sample was polished, sonicated in ethanol >30 min, rinsed in fresh ethanol, air dried, pretreated in acetic acid for 30 s, dipped in purged ACN for 5 s, and dried with Ar. Each of the four samples was placed in the XPS vacuum transfer chamber within 15 s of preparation. The O 1s line of the control sample is at 531.2 eV, indicating that the predominant oxidized species still remaining on the bare Cu is $Cu(OH)_2$. For a 10 s dip in the derivatization solution, two peaks at 530.5 and 531.8 eV were observed. The peak at 531.8 eV follows the same trend as spectra of derivatized native oxide Cu samples. The peak at 530.5 eV indicates a reversion of part of the sample back to its original native oxide upon exposure to the derivatization solution, as discussed below. A Cu Auger spectrum of this same sample, however, shows that Cu^0 is still the predominant state of the surface Cu. With the longer dipping times of 1 and 15 min, all the oxygen appears at the higher binding energy of 532.8-533.0 eV. Mukhedkar *et al.* observed the O 1s line at 532.8 eV in XPS spectra of Cu(2,4-pentanedione),[22] in which the oxygen atoms are present only in Cu(II)-O-C bonds. An additional example of a metal-O-C bond examined with XPS is noted in work by Dicke

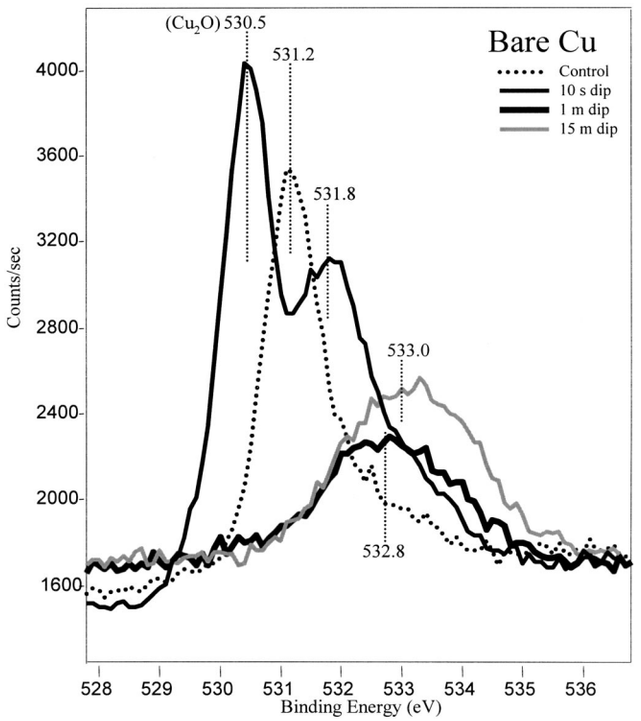

Figure 8. O 1s XPS spectra of bare Cu surfaces derivatized with increasing dipping times in phenyl diazonium salt solutions.

et al. in which the O 1s line at 532.0 ± 0.2 eV is assigned to oxygen in the Zr-O-C bond of bis(acetylacetonato) bis(1,1,1,3,3,3-hexafluoro2-propanolato) zirconium.[34] Therefore, data from both the native oxide Cu and the bare Cu provide strong evidence of the establishment of a Cu-O-C bond. Furthermore, to eliminate the possibility that the positive shift was caused by long exposure to ACN and/or other factors in the derivatization process, a separate control sample of bare Cu was prepared with a 30 s pretreatment in acetic acid, a 15 min dip in purged ACN, Ar jet drying, and immediate introduction into the XPS vacuum transfer chamber. The O 1s spectrum of this sample was virtually identical to that of the control sample in Fig. 8 with its predominant peak centered at 531.2 eV.

Although the origin of the 530.5 eV O 1s peak from the 10 s dip sample of bare Cu is not clear, two possibilities arise: (*i*) the formation of Cu_2O during the derivatization process or (*ii*) the formation of Cu_2O during the transfer to the XPS instrument. Some aspect of the derivatization process appears to be the cause of the formation of Cu_2O, however, as the control sample does not exhibit a peak at 530.5 eV.

Cu-C bond.—Proof of a Cu-C bond is not as direct as that for a Cu-O-C bond; however, the data in Table II (calculated from the spectra of the eight samples described previously) provide evidence of the establishment of such a bond. The C coverage observed with each of the derivatization times increases significantly faster on the bare Cu than on the native oxide Cu. After a 1 min dip of the bare Cu in the derivatization solution, 91% of the surface was carbon compared with only 54% for a 1 min dip of the native oxide. Furthermore, after a 1 min dip of the native oxide Cu, 19% of the surface is still Cu (presumably in the form of a copper oxide). After a 1 min dip of the bare Cu, however, only 1% of the surface is Cu. Both the 1 min and the 15 min dips of bare Cu appear to have films thick enough to prevent observation of photoelectrons from the Cu substrate. The Cu 2p spectrum of the 1 min bare Cu dip was extremely weak and that of the 15 min bare Cu dip showed no discernible Cu peak. The C 1s and the Cu 2p spectra of the bare Cu samples are shown in Fig. 9.

To remove any ambiguity arising from the combination of adventitious C and changes in C coverage on the samples derivatized with phenyl diazonium salt, XPS analyses were also performed on samples derivatized with nitrophenyl diazonium salt. Changes in the N 1s signal from the nitro group should follow the same trends as the C 1s signal from the phenyl ring under the various derivatization conditions. Samples derivatized with nitrophenyl diazonium salt were prepared in a manner identical to that for the above-described phenyl samples except derivatization took place in 3 mM nitrophenyl diazonium salt and only two dipping times were used for each of the two surfaces. Samples were dipped for either 5 or 20 s. The derivatization times are shorter with the nitrophenyl salt because the electron-withdrawing nitro group causes a more positive reduction potential and thus derivatization proceeds at a faster rate.[1] XPS spectra of samples derivatized with nitrophenyl diazonium salt exhibited two distinct N 1s peaks, one centered at 399.9 eV and one centered at 405.9 eV. These peaks are attributed to N in an azo group

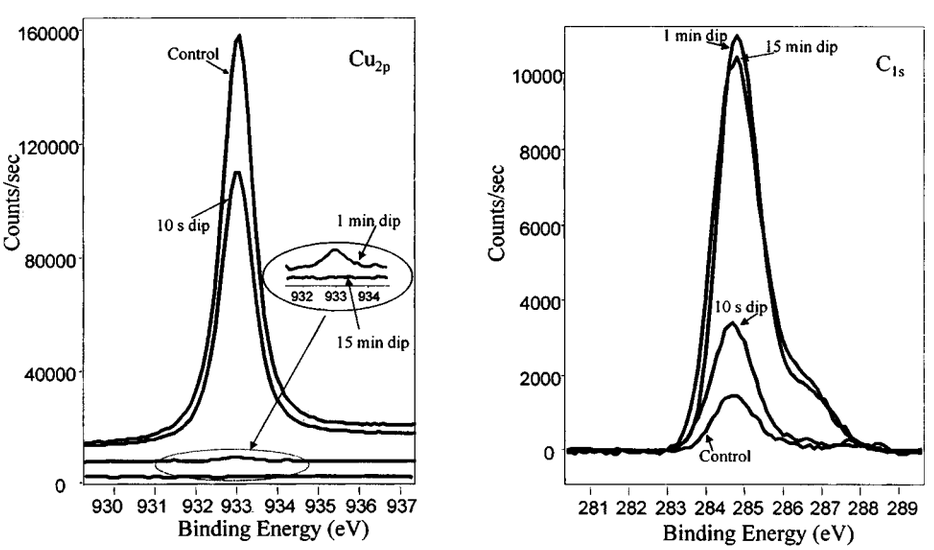

Figure 9. Cu 2p and C 1s spectra of bare Cu samples derivatized with phenyl diazonium salt. (2 pt baseline adjustment applied to C 1s spectra.)

Table III. Surface coverage of samples derivatized with nitrophenyl diazonium salt.

	% O	% Cu	% C	% N[a]	% N[b]
Control native oxide	26	38	36	<1	0
5 s native oxide dip	27	31	39	<1	2.1
20 s native oxide dip	28	14	53	1.9	3.7
Control bare Cu	6	71	22	<1	0
5 s bare Cu dip	16	5	69	2.9	6.5
20 s bare Cu dip	16	4	71	3.7	6.4

[a] Using the integrated area from 398 to 402 eV, attributed to N in azo groups.
[b] Using the integrated area from 404 to 408, attributed to N in nitro groups.

and N in the nitro group, respectively.[35,36] Table III shows that both the C 1s signal and the N 1s signal from these samples follow the same trends observed with the samples derivatized with phenyl diazonium salt. The surface coverage of N from the nitro group is higher on the derivatized bare Cu samples and the percent Cu that can be analyzed through the film drops sharply as the film apparently thickens on the bare Cu samples. Comparison of the surface coverage of C on the two different surfaces also follows the same trend as the samples derivatized with phenyl diazonium salt. This additional information is entirely consistent with the conclusions reached in the phenyl case. The increased coverage and thickness of films formed on bare Cu surfaces gives good, but not conclusive evidence of the formation of a Cu-C bond. Another indication that there is a difference in the majority type of bond formed on the two different surfaces is discussed below.

Multilayer formation and azo coupling.—Assuming a film density of approximately 1070 kg/m^3 and using Seah and Dench's formula for attenuation length through an organic film, the approximate minimum escape depth for a Cu 2p electron with a kinetic energy of 554 eV is 24 Å.[37,38] The gradual loss of signal from Cu 2p electrons from samples derivatized with increased dipping times, therefore, is a clear sign of the formation of multilayers. The two types of bonds expected to occur in the multilayer formation of phenyl diazonium salt on Cu are shown in Fig. 10. After formation of the initial monolayer, C-C bonding between two phenyl rings is the most likely type of bond to form. This occurs when the diazonium cation in solution accepts an electron, loses N_2, and the resulting radical attacks the para position of an attached phenyl ring. The source of electrons for

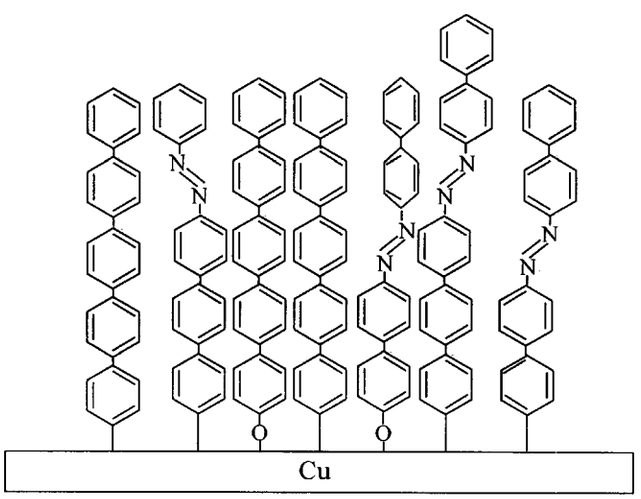

Figure 10. Formation of multilayers on a Cu substrate derivatized with phenyl diazonium salt.

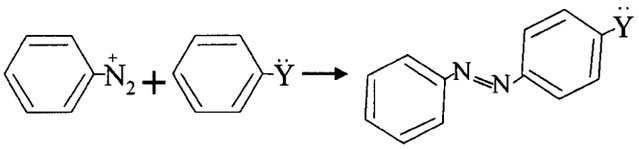

Figure 11. Azo coupling reaction in solution. Y = -OH or -NR_2.[23]

this reduction is presumably metallic copper. Although the specific mechanism is unknown, electrons can either tunnel through the attached phenyl layer or be conducted through the conjugated π system via a variety of conduction mechanisms.[23,39,40] Another bonding possibility is azo coupling of the diazonium cation with an attached ring. Figure 11 shows the coupling reaction that diazonium salts undergo in solution, in which the diazonium cation attacks only an electron-rich ring (Y = −OH or $-NR_2$).[41] In the current experiments, Y is replaced with the entire Cu substrate, and therefore the attached phenyl ring would also be expected to be electron rich. Furthermore, both the initial monolayer and subsequent layers would be expected to be more electron rich in the case of the Cu-C bond than in the case of the Cu-O-C bond. Based on this assumption, analysis of the presence of azo groups in the film supports the establishment of a Cu-C bond.

The presence of an ~400 eV N 1s signal in the nitrophenyl-modified samples (Table III) indicates that some azo nitrogen is also incorporated in nitrophenyl-derived films. Therefore, azo group analysis was performed on both the phenyl- and the nitrophenyl-derivatized samples. As noted previously, the N 1s spectra for nitrophenyl samples contained two distinct peaks, and the N 1s spectra for phenyl samples contained only one peak. A peak centered at 399.9 eV is attributed to N in azo groups and one centered at 405.9 eV is attributed to N in nitro groups.[35,36] The possibility of an N 1s signal arising from unreacted diazonium salt was eliminated as such signal would produce two peaks at 403.8 and 405.1 eV, which was not observed.[42] The relative coverage of azo groups and phenyl rings in the organic layers formed from both phenyl and nitrophenyl diazonium derivatization was determined using the same data used to calculate surface percentages in Tables II and III. Table IV shows that for both salts, derivatized bare Cu surfaces contained a higher percentage of azo groups than derivatized native oxide Cu surfaces. Particularly noteworthy are the data from the 15 min native oxide phenyl diazonium dip and that from the 1 min bare Cu phenyl diazonium dip. Both these samples appear to have relatively thick films based on the low percentage (1%) of Cu apparent on the surface. The film on bare Cu, however, contains one azo group for every 5.9 phenyl rings, while the film on native oxide Cu contains one azo group for every 17.4 phenyl rings. The difference in the coverage of azo groups is evidence that the formation of multilayers on bare Cu proceeds in a manner different from that on the native oxide surface. The nature of the initial bond to the substrate could account for this difference, via its effect on electron transfer through the initial monolayer.

Finally, it is unlikely that the azo group would bind directly to the substrate forming a Cu-O-N bond or a Cu-N bond. The success of the Sandmeyer and Gattermann reactions indicates that either Cu^{+1} or Cu^0 quickly reduces the diazonium cation to produce N_2 and the radical. Additionally, if the azo group were attached to the surface, the two N atoms would most likely produce separate peaks in XPS analysis, which was not observed. Furthermore, if the azo group were attached directly to the substrate, the percentage of N on the samples derivatized for short periods of time should show a relatively higher percentage of N than those that were derivatized for long periods and formed multilayers. As Tables II and III show, a higher N/C surface ratio was not observed for the thinner films.

As noted earlier, copper was studied in detail because of its cathodic activity in Al/Cu alloys and its association with galvanic corrosion in aircraft alloys. Although preliminary, the results of the

Table IV. Number of phenyl rings per azo group contained in multilayers on Cu surfaces.

	Native oxide Cu surface phenyl rings/azo group	Bare Cu surface phenyl rings/azo group
1 m phenyl diazonium dip	16.5	5.9
15 m phenyl diazonium dip	17.4	5.4
5 s nitrophenyl diazonium dip	13.8	8.1
20 s nitrophenyl diazonium dip	9.4	6.4

diazonium modification of AA-2024 T3 shown in Fig. 6 are encouraging with respect to possible organic modification of aircraft alloys. The strong Raman signal and stability in boiling water imply strong surface bonding and high coverage. Because only approximately 4% of the alloy surface is copper, it is likely that the main bonding mechanism involves an Al-O-phenyl linkage. Bonding to Al or Al oxide rather than Cu or Cu oxide may account for the apparently greater stability of the organic film on AA-2024 T3 compared to copper. The absence of an observable intensity change in the Raman spectra of nitroazobenzene on AA-2024 T3 upon treatment in boiling water implies that binding of the organic film is stable to hydrolysis.

Conclusions

Derivatization of Cu substrates with aryl diazonium salts can be achieved in both aprotic and aqueous media at OCPs. The bond formed in both media remains stable under vigorous testing, indicating a covalent bond. The O 1s XPS spectra of native oxide Cu and bare Cu samples derivatized with phenyl diazonium salt under aprotic conditions give strong evidence for the formation of a Cu-O-C linkage between the substrate and the phenyl ring. Azo coupling within the multilayer is consistent with solution-phase azo coupling of diazonium salts with electron-rich aromatic rings. Comparisons of surface coverage for both phenyl and nitrophenyl diazonium salts along with differences in the percentage of azo groups formed in multilayers on the two different surfaces provide good evidence for the establishment of a Cu-C bond. The multilayer structure shown schematically in Fig. 10 indicates the presence of both Cu-C and Cu-O-C bonding, as well as incorporation of azo groups, consistent with experimental observations. The mono- or multilayer thickness of the organic layer is a function of both the diazonium ion structure and the deposition conditions.

Although Cu holds a unique relationship with diazonium salts, these qualities could be expected to apply to other metal substrates, albeit to a different extent. This would be particularly true in the case of Sn, Cr, Ti, V, and Fe, whose cations are also used as catalysts in dediazoniation reactions.[21] In addition to corrosion inhibition, derivatization of these metal substrates with an almost endless selection of functionalized diazonium salts could be valuable in biomedical and molecular electronic applications.

Undoubtedly, replacing chromate-based corrosion inhibitors involves first the determination of viable alternatives, next the refinement of the many possible steps in each alternative, and then finally further refinement of each step. The derivatization of metal substrates with aryl diazonium salts at OCP in an aqueous medium provides a fast, simple method for attaching organic multilayers on metal surfaces with minimal waste disposal issues. Further research needs to be undertaken to determine whether this type of derivatization by itself will inhibit corrosion, but the numerous choices of molecules available and the option of combining this type of derivatization with other inhibition methods provide good reasons to pursue this method as a viable alternative to chromate corrosion inhibitors.

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